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The impact of fuel properties on the emissions from the combustion of biomass and other solid fuels in a fixed bed domestic stove

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ABSTRACT

Experimental results are presented on the emissions from a single combustion chamber stove burning wood, coal and processed fuels. This technique was used to permit comparisons to be made of the influence of different fuel types without it being influenced by the effects of secondary combustion. Measurements were made of CO, NO_x and fine particulates during the major phases of combustion, namely flaming and smouldering. Measurements of the particulates were made in two ways: firstly using a gravimetric total particulate measurement and secondly using a cyclone technique to give $PM_{2.5}$ and PM_{10} size fractions. Smoke emissions from the different fuels were very dependent on the phase of combustion especially for the total particulate results, where flaming phase emissions were much higher than in the smouldering phase. It was found that the particulate emission factors for the wood fuels were dependent on the volatile content whilst the coals followed a different pattern. NO_x was linearly dependent on the fuel-N content for all the fuel types, but the relationship for biomass is different from that for coal. CO emissions were very dependent on the combustion phase.

1. Introduction

A number of countries have introduced energy policies in order to reduce greenhouse gases. In the case of heating applications this has led to an increase in the use of wood burning stoves and boilers particularly in Europe, although coal burning appliances are still widely used in many parts of the world. The use of solid biofuels has been the fastest growing energy source in the UK in the last two decades and a similar situation applies across the EU. In many cases these appliances use a single combustion chamber originally designed for the combustion of coal and often the combustion process is poorly controlled. More recently stoves designed specifically for biomass fuels and employing better fuel preparation have reduced the extent of the emissions. Nevertheless there are still concerns about the health effects particularly from fine particles and NO_x [1–5] as well as from the influence of black carbon and organic compounds on climate change [6,7].

In the UK the Renewable Heat Incentive (RHI) [7] has been promoted for both domestic and commercial application which advocates the use of low carbon technologies including the use of biomass fuels. Similar schemes operate in many parts of Europe; in Ireland a combination of higher prices and policies such as the Greener Homes Scheme has resulted in a greater use of wood for domestic heating. The UK Clean Air Act and RHI [8] place emission limits on small appliances when tested to standard methods (BS PD 6434 and BS EN 303-5). A variety of emissions limits or test standards operate around the world. In the EU there is a proposal to bring in much tighter legislation by 2022 (Eco-design) for solid fuel local space heaters, with particulate emissions and NO_x varying according to fuel type. The emphasis on emissions is currently directed to both fine particulates and NO_x. Many of the particles produced are below 1 μm in diameter which are the most hazardous to health [1]. Wood burning is also associated with high emissions of organics such as polycyclic aromatic hydrocarbons (PAH) which are known to be mutagenic and carcinogenic [2–4]. Consequently a number of research programmes have looked in detail at the emissions from wood-fuelled appliances [3,9–18] and there is also interest in pre-processing the fuels to reduce emissions.

In this paper we have used a fixed grate stove with a single combustion chamber. This type of stove has the advantage of giving information on the emissions directly released from the primary combustion of the fuel enabling the effects of different fuel types to be studied. Thus we have studied a range of fuels, two woods, a torrefied fuel, a peat, a biomass/coal blend and two smokeless fuels. This design is still widely used in many countries for domestic heating. Measurements were made of the particulate and gaseous emissions during a single combustion cycle for a number of fuels used typically in the UK and Ireland in order to obtain insight into the effects of the different phases of combustion, flaming and smouldering, on pollutant formation. A flue gas sample dilution tunnel was

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not used because of the diverse fuels studied and so information was obtained only on the primary products formed.

2. Experimental methods

2.1. Fuels used

A total of eight fuels were studied which are listed in Table 1. They consist of three groups; (1) two woods, these having similar moisture levels to avoid the complications resulting from too many variables, (2) a pre-treated biomass fuel and (3) coal or coal derived fuels, these being included for comparison purposes. Biomass fuels were shredded using a Retsch SM100 cutting mill to a size of <1 mm, and were then milled using a SPEX 6770 cryogenic grinder to achieve a very fine particle size required for analysis. The mineral fuels were milled using a Retsch PM100 ball mill. All samples were sieved to ensure a particle size of 90 μm or less. The wood logs were milled and analysed including the bark.

Proximate analysis on the coal and smokeless fuels was carried out according to BSO ISO 17246. For the biomass fuels, proximate analysis was carried out according to BS EN 14774-3 for moisture, BS EN 15148 for volatile matter and BS EN 14775 for ash. These are the same as for mineral fuels, but the moisture was determined in air rather than nitrogen, and the ashing temperature is 550 °C rather than 815 °C. The 50:50 blended fuel was tested both ways for comparison purposes. Ultimate analysis (CHNS) was carried out on a CE Instruments Flash EA1112. Gross calorific values (GCV) were determined on a weight % dry basis by bomb calorimetry using a Parr 6200 Calorimeter. Cl and P were determined via ion chromatography of the washings following bomb calorimetry. This method is in accordance with Method A of BS EN 15289:2011. The P and Ca values were determined by means of nitric acid digestion and ICP-MS, and K values were determined using atomic absorption spectroscopy (AAS) since it is more accurate than ICP-MS. The data obtained are given in Table 2. VM denotes volatile matter and FC the fixed carbon content.

2.2. Combustion experiments

A fixed bed stove (Waterford Stanley Oisin) was used which meets the current designs to use multiple fuels. The appliance is nominally rated as having a maximum non-boiler thermal output of 5.7 kW and an efficiency of 79% and in these experiments the unit was run at approximately full load. A diagram of the unit and the flue and sampling arrangements are shown in Fig. 1. The internal dimensions of the combustor are 250 × 270 × 190 mm (height × width × depth) with a deflector plate across the top section. The geometry of the combustion chamber was unchanged in all the experiments. There is a single primary air supply under the grate which is manually controlled via a damper. The dimensions of the grate which determines the distribution of the air flow as well as the movement of the fuel particles and ash in the burning bed are shown in Fig. 2. The stove was mounted on an electronic balance and the general arrangement of the test equipment was largely in accordance with BS EN 13240. Each run was started using the stove at room temperature to replicate a cold start.

Sampling was undertaken by means of ports in the flue positioned 1.43 m above the stove as shown in Fig. 1. The insulated flue had an internal diameter of 125 mm. The stove was directly underneath a laboratory extraction system which applied a continuous draught of 12 Pa as required for the nominal heat output test in BS EN 13240.

A weighed batch of fuel which was in the range of 2–3 kg was used for each run, with no re-loading being undertaken; this mass was chosen on the basis of BS13240 and the nominal heat output and efficiency. As far as possible the fuels were placed on the grate in a similar way each time with a uniform level bed layer. The sizes of the fuels are given in Table 1. All of the briquetted fuels were approximately the same size and logs of a similar size were selected but in this case there was a greater variation. There are some small deviations from the strict application of the standard method (such as the diameter of the flue) but in these experiments using a small stove the objective is to compare fuels using combustion of a single batch of fuel. The primary air flow was adjusted on the basis to give 100% excess air for the coal-based fuels and 150% for the biomass fuels as recommended by the manufacturer for this stove. Ignition was undertaken by means of a known mass of firelighters which were arranged in the same position on the grate for each experiment. The early part of the ignition phase is influenced by this process and these results are not included.

Flue gas samples were taken when ignition was complete and combustion established. Their composition was measured using a Testo 340 instrument for O_2, CO_2, CO, NO, NO_2, SO_2 as well as the flue gas temperature. The accuracy of the gas composition measurements was ±5%. Flue gas velocity and flow rate were measured using a Wöhler DC100 computer for pressure measurements and an S-type pitot tube, in accordance with BS EN ISO 16911-1.

The particulate content in the combustion gases was measured in two ways. In the first, PM_{10} and $PM_{2.5}$ were determined using a cyclone set (US EPA Method 201a and BS ISO 25597). Here a sampling probe consisting of cyclones, a pitot tube and a thermocouple is inserted directly into the flue. Flue gas is drawn through the sampling nozzle into the cyclone separators and then through a heated line into a set of impingers to collect water and other condensables, and then to a dry gas metre. The cyclones were mounted externally to the flue at a controlled temperature of 170 °C. As far as possible isokinetic sampling was used but with the low flow rate in the flue (<1.5 m s^{-1}) this was difficult and is not necessary for the relatively small particulate sizes [19]. Sampling was carried out for a period of typically 20 min for each fuel. The filters were stored at 5 °C prior to analysis.

In the second method, total particulate matter (PM_t) was determined using a gravimetric method which required 25 L of sampled gas passed through a Whatman GF/F glass microfibre (0.7 μm) filter paper, with a second one used as a backing filter paper. The gas was taken via a heated line at 120 °C and passed through the filter papers which were in a holder mounted on a furnace at 70 °C. The furnace arrangement permitted the gases to be cooled to this temperature and permitted the condensation

Table 1
Fuels types used in the study.

Fuel no.	Fuel type	Physical description
1	Domestic firewood (A)	Commercially available seasoned mixed hardwood. ~200 mm long; diam. ~70 mm
2	Domestic firewood (B)	Air dried hardwood (silver birch) logs, ~200 mm long; diam. ~70 mm
3	Torrefied wood briquettes	Torrefied spruce wood (bark-free). Briquettes approx. 70 mm diameter. From Andritz AG. Torrefaction temperature approx. 280–295 °C.
4	Peat briquettes	Briquettes of pressed peat. Length ~185 mm diam. ~70 mm
5	Bituminous coal	Premium grade bituminous coal (Poland) supplied in lumps ~100 mm
6	Biomass/coal blend	Briquetted blend of 50% olive stone/50% low sulphur petroleum coke, coal and anthracite. Approx. 80 mm diameter
7	Low smoke fuel	Cosyglo (supplied by Arigna Fuels). Anthracite based commercially available product, 84 × 65 × 35 mm briquettes.
8	Smokeless fuel	Ecobrite (supplied by Arigna Fuels). Anthracite based commercially available product, 50 × 50 × 30 mm briquettes.

Table 2
Proximate and ultimate analyses and gross calorific values (GCV) for the fuels used.

Fuel no.	1	2	3	4	5	6	7	8
Fuel type	Wood A	Wood B	Torrefied briquettes	Peat briquettes	Coal	Biomass blend	Low smoke	Smokeless
VM (% db)	84.2	79.3	72.1	64.4	39.7	14.0	23.4	8.2
Ash	0.1	0.9	1.0	4.9	4.2	6.7	5.5	5.2
FC	15.8	20.5	27.6	33.4	57.9	80.1	72.1	86.9
MC (% ar)	8.4	7.8	4.6	7.1	7.2	2.7	6.3	3.4
C (% daf)	53.3	51.6	54.7	59.1	82.1	74.3	78.0	81.6
H	6.1	5.9	5.8	5.0	4.8	3.6	3.9	3.4
N	0.4	0.6	0.1	1.6	1.9	1.7	1.6	1.7
S	0.03	0.02	0.04	0.4	0.4	2.1	0.4	2.0
Cl (% db)	0.03	0.02	0.04	0.11	0.06	0.05	0.05	0.02
P (ppm db)	3591	4142	4059	3750	3608	4815	3980	3629
Ca	18,386	11,978	8766	27,244	5923	10,261	16,375	5867
K	583	3487	1280	89	265	11,168	723	767
Zn	140	823	55	47	1	0	21	0
GCV (MJ kg^{-1} db)	19.5	18.8	23.0	20.6	36.3	27.6	34.5	33.3

ar = as received; db = dry basis; daf = dry ash free.

of semi-volatile organic compounds. The filter temperature was chosen to be the same as that recommended in the dilution tunnel standard [BS 3841]. Three repeat measurements were taken in each combustion phase for each fuel and the arithmetic mean average reported. Each sample was taken for 5 min before the filter papers were changed. All filter papers were stored in a desiccator for 24 h prior to measurement. Particulate matter was examined using a Hitachi SU8230 scanning electron microscope (SEM). Samples were platinum coated.

Values of elemental carbon (EC) and organic carbon (OC) were determined using a thermo-gravimetric method (TGA) which yields time-weighted-average measurements. The Total Carbon (TC) is the sum of EC and OC. This method was adopted because in this study there was a very high particle loading on the filters which rendered them unsuitable for thermal/optical analytical methods. Thus we used a TGA with a nitrogen carrier gas and we assume that OC is equivalent to the volatile content (105 °C — 550 °C in N_2) and EC is equivalent to the fixed carbon content (550 °C in air). It allows accurate comparisons to be made between the different soot samples.

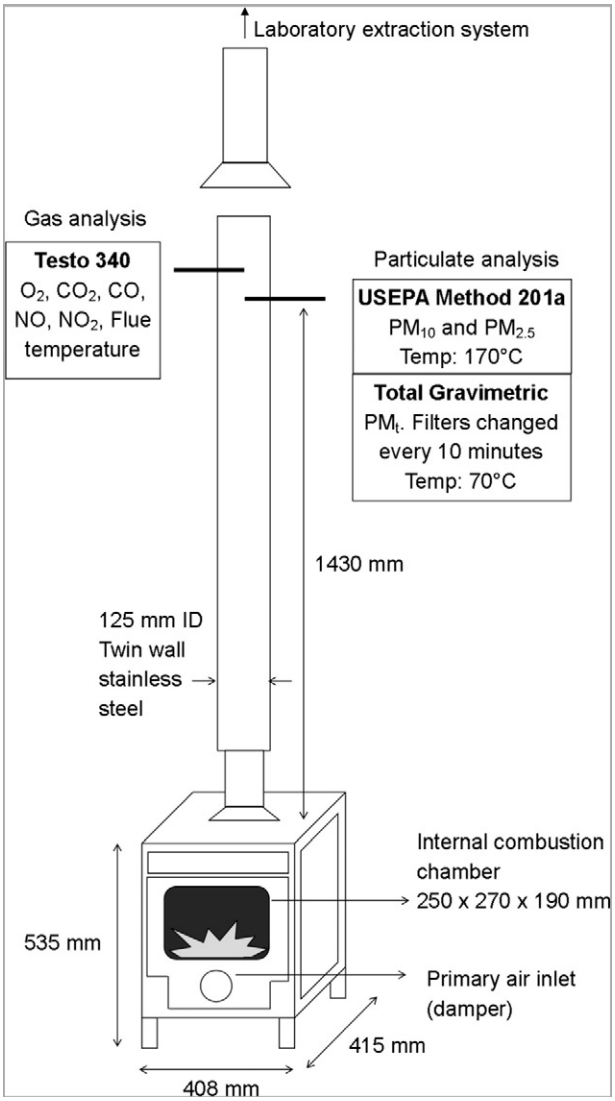

Fig. 1. Diagram showing the equipment arrangement.

3. Experimental results

3.1. Fuel properties

Thermogravimetric analyses (TGA) were made on all the fuels. The heating rates used were those employed for the determination of the proximate analysis based on the BS methods. The TGA results obtained are shown in Fig. 3 together with the heating profiles employed.

The proximate, ultimate, and gross calorific value (GCV) results for each fuel measured in the conventional way presented in Table 2 are consistent with the TGA plots. There were difficulties in the

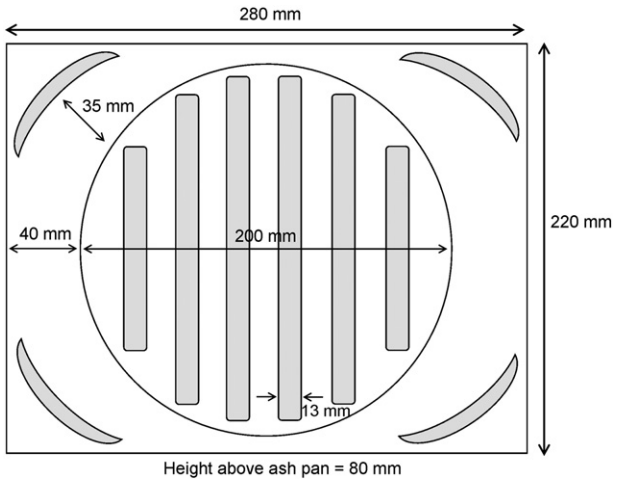

Fig. 2. Diagram showing the grate arrangement.

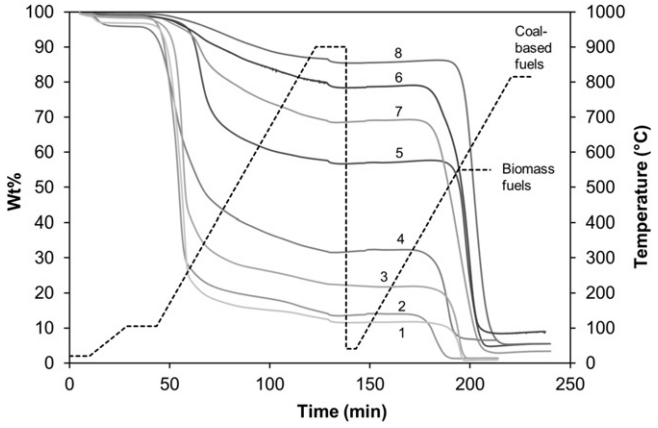

Fig. 3. TGA results for the fuels studied. 1: wood A; 2: wood B; 3: torrefied wood briquettes; 4: peat briquettes; 5: coal; 6: coal/biomass blend; 7: low smoke fuel; 8; smokeless fuel. Temperature —.

measurement of some of the quantities because of their inhomogeneous nature, for example, the wood samples contained bark whilst the biomass/coal mixture contained components of greatly differing VM content. However the trends are important and are clearly identified. Of particular note in Fig. 3 and Table 2 is the trend in the volatile content with the woods having the highest values and the smokeless fuel having the lowest value.

Batch combustion in a fixed bed follows three major stages. Ignition occurs first once the surface material of the fuel devolatilises and forms a gaseous flame. Once this flame is established the 'flaming phase' takes place characterised by the combustion of volatile products and their decomposition products (secondary pyrolysis products) as luminous diffusion flames. Thirdly the smouldering phase occurs which is characterised by heterogeneous char combustion and limited visible gas phase combustion. Elasser et al. [17] have recently identified four combustion phases but in the present work we have used the simpler classification of the two major phases, flaming and smouldering because of the difficulty of distinguishing between the other phases.

Measurements were made of the mass burning rates for all fuels and these are shown in Fig. 4. These are consistent with the TGA results shown in Fig. 3. The initial maximum value is followed by a decline

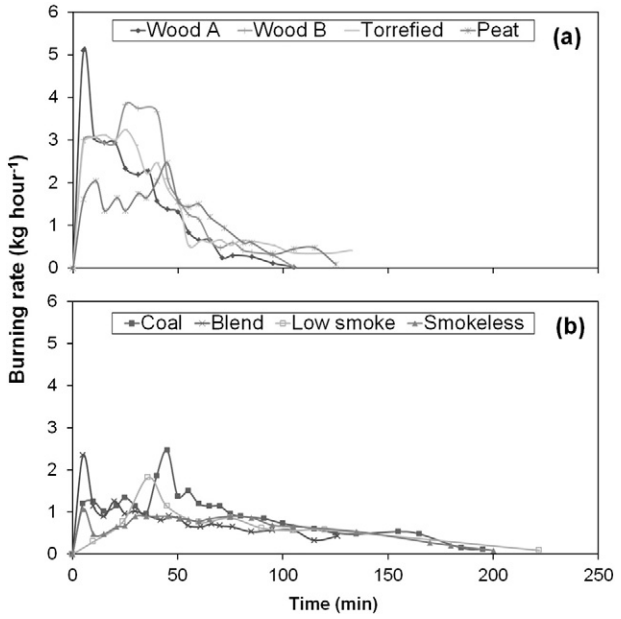

Fig. 4. Variation of burning rate with time for each of the fuels. (a) fuels 1–4; (b) fuels 5–8.

with occasional slight increases due to the movement of the fuel in the bed. The time during a combustion cycle at which samples are taken for particulate analysis was found to have a substantial influence on the emission data. It is interesting to note that the high volatile wood fuels release a high concentration of highly carbonaceous dark smoke during flaming combustion. In contrast the torrefied fuel burns more slowly and has a more uniform rate of heat release and of smoke emission.

The average burning rates for the flaming and smouldering phases for all the fuels are given in Table 3.

As expected the flaming rates are approximately proportional to the volatile content (VM) since they are dependent on the volatile matter released whilst the smouldering rate is proportional to the Fixed Carbon (FC) values given in Table 2. The flue temperatures reflected the burning rates and approximately followed the same pattern with time and their values ranged from 150 to 350 °C.

3.2. NO_x and SO_x emissions

NO_x measurements were made throughout the combustion cycle. NO_x emission factors were calculated for both flaming and smouldering phases on the basis of 13% O_2 content in the combustion gases. These values are given in Table 4 where the errors are ±10%. The values averaged over the whole cycle are also given.

The NO_2 content was always less than 5 mol% for the biomass and 15 mol% for the coal based fuels. The emission factors vary significantly with the fuel-N content; the values for the nitrogen content of the biomass fuels (<0.6 wt.% daf) is much lower than for the coal and peat samples. Plots are given for the emission factors for both phases in Fig. 5.

It is seen that the NO_x emission factors for each fuel are dependent on the phase of combustion, that is, whether it is flaming or smouldering, although the effect is not large. The variation with fuel-N content is interesting because they are dependent only on the fuel-N content and not on the fuel type. It is well known that NO_x emissions from coal combustion [20] and from biomass combustion [21] are a function of the fuel-N content but it has not been shown that the emissions from all these fuels follow the same linear relationship for combustion in a stove. This probably arises because the fuel-N present in all these fuels consists mainly of cyclic N-compounds and so the formation of NO. A similar situation will also hold for the conversion during the smouldering period where the common feature is the char-N. The NO_x emissions predominantly resulted from fuel-NO_x because relatively small amounts of thermal NO_x are formed in the residence times available in either the flaming or smouldering phase. The evidence for this comes from (a) on the basis of a calculated residence time of 0.2 s and an average combustion chamber temperature of 1500 K then the computed NO_x yield is 1 ppm using the method used by us previously [22], (b) CFD calculations for a similar wood furnace but at a higher temperature gave a value of 25 ppm [23].

The sulphur content varies between 0.02% for the wood fuels to 2.0% for smokeless fuel (no. 8) whilst the 50:50 test fuel (no. 6) has a sulphur content of 2.1% which has implications for SO_x emissions. The consequence is that the equilibrium SO_2 concentrations are about 50 ppm

Table 3
Average burning rates during flaming and smouldering phases for the different fuels.

Fuel	Average burning rate (kg h^{-1})	
	Flaming	Smouldering
1	2.37	0.27
2	2.59	0.32
3	2.59	0.47
4	1.61	0.36
5	1.31	0.43
6	1.05	0.58
7	0.99	0.42
8	0.77	0.54

Table 4
NO_x emissions factors for the different combustion phases.

	ppm at 13% O_2		mg MJ^{-1}		
Fuel	Flaming	Smouldering	Flaming	Smouldering	Average over whole cycle
1	88	40	152	67	110
2	98	54	175	93	142
3	74	32	134	56	85
4	274	190	504	345	438
5	184	105	274	153	204
6	216	237	367	401	390
7	219	161	345	253	287
8	195	167	292	249	259

for the woods whilst the values from the coal based fuels are in the range of 350 to 1500 ppm. The wood ash was studied using energy-dispersive X-ray spectroscopy (EDX) and this showed relatively low unburned carbon content and a high presence of Si, Ca and K. Some of the SO_2 is retained by the ash forming calcium compounds and the flue gases contained less than the calculated equilibrium amount and typically 10 ppm SO_2 was found experimentally.

3.3. Particulate matter emissions

The PM emissions factors for each fuel are dependent on the fuel studied also on whether the fuel is flaming or smouldering. A typical plot of the fuel burning rate and the total particulate emission (PM_t) from the combustion of the torrefied wood (no. 3) as measured by the gravimetric method is shown in Fig. 6(a). The distinction between the flaming and smouldering phases is best done by direct visual observation and it coincides with a change in the CO and NO_x emissions as shown in Fig. 6(b). The change is gradual and often complicated by random movement of the burning fuel bed despite keeping the combustion conditions as similar as possible. This can result in errors in defining the phases of combustion.

Particulate samples were taken periodically during the combustion cycle and the weight of the sample determined at the points shown in Fig. 6. Each point represents a sample taken over a 5 min period. The total particulate measured for each combustion phase is the average of

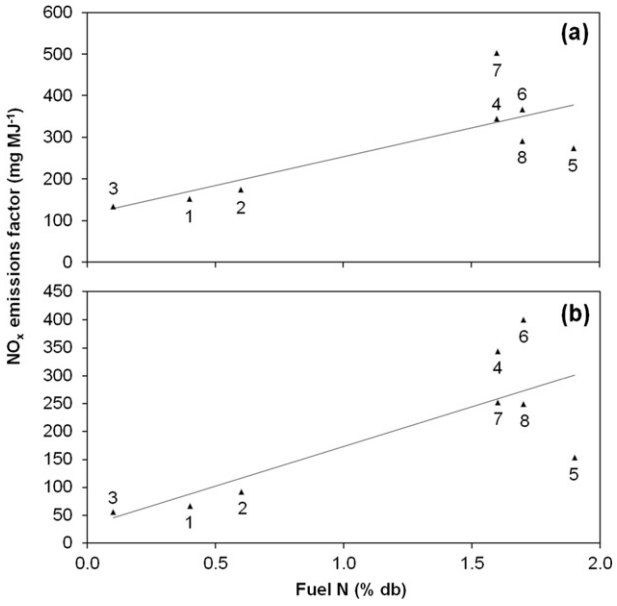

Fig. 5. NO_x emissions for each fuel plotted against fuel nitrogen content for (a) flaming, and (b) smouldering phases.

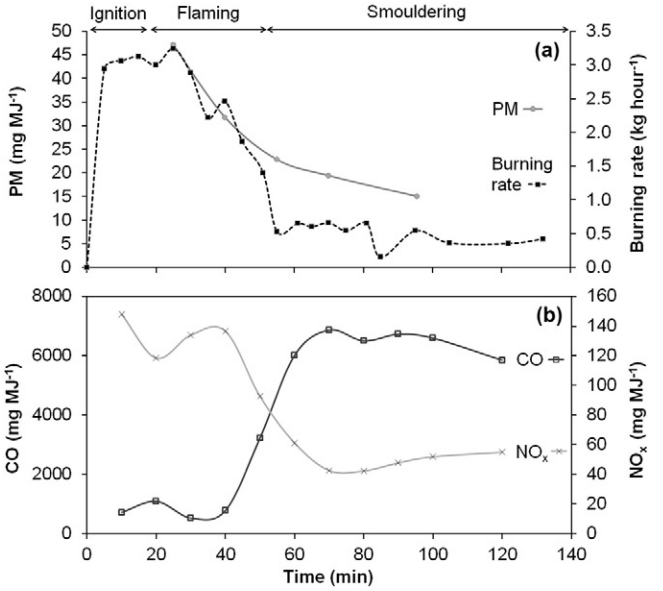

Fig. 6. The variation of (a) the burning rate, ■, and emission factors for PM, ●, and (b) emissions factors for CO, □, and NO_x, ×, for the burning of torrefied wood briquettes (fuel no. 3).

the values in that region. It was found that the particulate samples consist of two components: a carbonaceous black smoke which deposits on the first filter paper and a yellowish material containing potassium that is collected on the second (backing) filter paper. The material on the second filter paper must have a particle size less than 0.7 μm. It was also noticed that the smoke on the first filter paper of the second sample taken just after the peak of devolatilisation was brownish in colour, in contrast to all the other samples which were black. This brown soot (brown carbon) is tar-like rather than particulate as is the case with the black soot.

The PM_t emission factors measured by the gravimetric method for the different fuels are given in Table 5 for the different combustion phases. They are presented in terms of mg m^{-3} at 70 °C which is the temperature at which they were measured. The results show a substantial difference between PM emission rates in the flaming and smouldering phases. Average figures over the whole of the combustion cycle are also given. There is also a difference in the ranking of the fuels, depending on the basis used for comparison. The results on an energy basis are shown in Fig. 7.

The trends are quite marked since the PM released during the flaming phase is much greater than for smouldering but the differences are much reduced in the case of the 'smokeless' fuels, torrefied wood and the smokeless coal. The experimental errors in these values are ±10%. The PM emissions in both phases for the two woods (nos. 1 and 2) are

Table 5
PM_t emissions factors for the two combustion phases as determined by the gravimetric method for all of the fuels.

	mg m^{-3} (as measured, 70 °C)		
Fuel	Flaming phase	Smouldering phase	Average over whole cycle
1	81	10	45
2	145	21	83
3	37	9	23
4	151	14	83
5	515	26	271
6	151	44	97
7	66	22	44
8	29	11	20

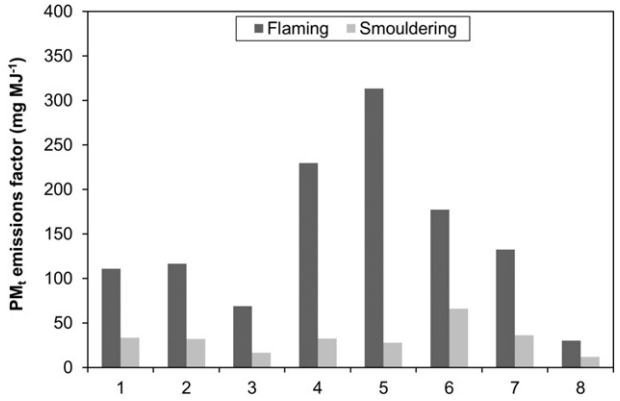

Fig. 7. Comparison of total particulate (PM_t) emissions factors from the flaming and smouldering phases using the gravimetric method for the different fuels (fuel nos. 1–8).

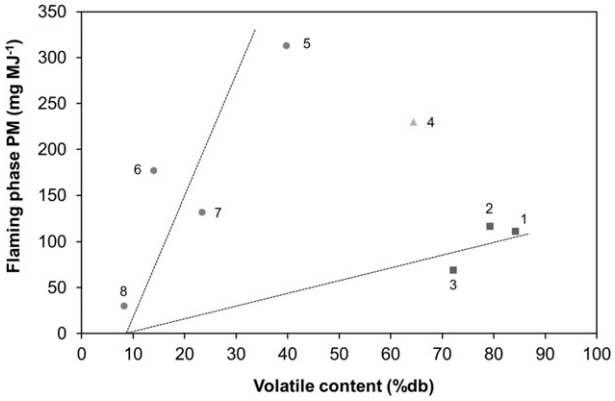

Fig. 8. Plot of the average flaming phase particulate emission (PM) against the volatile content (VM) for the fuels.

similar on a thermal basis whilst the value for the torrefied wood (no. 3) is much smaller. The coal (no. 5) gives the highest value with the peat (no. 4) and the blend (no. 6) giving intermediate values. The low smoke fuel (no. 7) is similar to the wood and the smokeless fuel (no. 8) is similar to the torrefied woods.

The size fractions PM_{10} and $PM_{2.5}$ were determined for some of the fuels using the cyclone method as well and the results for the flaming phase are presented in Table 6.

It is shown in Table 6 that there are significant differences in the emission factors reported by the two methods. Four fuels have been selected, a wood, a torrefied wood, peat and a smokeless coal, which have significant differences in their volatile content. The major factor resulting in the difference in the particulate emission factor by the two methods is in the choice of particulate collection temperature. The cyclone method which is at 170 °C would largely collect elemental carbon (EC) whilst the gravimetric method at the lower temperature of 70 °C will also collect involatile organic matter such as the PAH compounds (i.e. TC which is the sum of EC and OC.). Here we have taken the values for $PM_{2.5}$ (assumed to be mainly produced in the flaming phase) as well as the values form the gravimetric from the flaming phase (taken from Table 5 but shown here for comparison purposes). In principle this should give values for Elemental Carbon (EC) / Total Carbon (TC). In the case of wood (no. 1) this method gives a value of 0.8 ± 0.1, in the case of the torrefied wood (no. 3) and the peat (no. 4) both give 0.9 ± 0.1, and for the smokeless fuel (no. 8) a value of 0.5 ± 0.1. The significance of these values is discussed later.

The results from the cyclone tests also show that a very small amount of PM greater than 2.5 μm was collected for any of the fuels. This is consistent with observations which show that the majority of particles are below $PM_{2.5}$ and even PM_1 for example, as shown in references [9,18]. These soot particles are fragile and can easily fragment once they enter the atmosphere. This has been verified by electron microscopy studies of the particles on the filter papers. The individual particles were between 50 nm and 90 nm but are aggregated in the form of chains. Larger particles can be formed by the formation of loosely bound carbonaceous aggregates and this is much more marked with the coal particulates than for the biomass particulates. As a result there is a visible difference between the soot collected from mineral-based fuels and woody fuels.

Plots were made of the average total particulate against volatile matter (given in Table 2) and this is shown in Fig. 8. The origin is set at 9% VM because it is the value for coke which does not produce smoke during combustion [24]. The data consist of two main groups. The woods (nos. 1–3) lie on one line, the coal based fuels (5–8) lie on a different line and produce more smoke. The single point for peat (no. 4) lies in an intermediate position.

As is well known the total particulate mass from the combustion of biomass and coal consists of both carbonaceous soot and inorganic aerosols, the contribution of the latter from coal combustion is relatively small. In the case of the combustion of wood no. 1 the grate losses were measured and it was found that 1.0 g of ash was left from the initial 3.0 kg of fuel and the unburned carbon in the ash was less than 10 wt.%. Using the data in Table 2 it is seen that some of the ash in the original fuel is lost and if this is mainly due to evaporation of the potassium salts into the of combustion air, it would give a concentration of aerosol of 10–20 mg MJ^{-1}. This is consistent with the results of other research e.g. [18]. Thus in this work with a single stage combustor the carbonaceous soot is the dominant particulate emitted. The plot in Fig. 8 is therefore that of the carbonaceous particulate matter and it can be seen that the plot for the biomass fuels (nos. 1, 2 and 3) and the coal-based fuels lie on different lines. Peat (no. 4) which is partially coalfield has a degree of coalification intermediate position between the coal and the biomass, which it has in the plots in Fig. 8. These results are consistent

Table 6
PM_{10} and $PM_{2.5}$ emission factors for selected fuels by the cyclone method at 170 °C and comparison with the gravimetric method at 70 °C.

	Emission factor (mg MJ^{-1})		
	Cyclone		Gravimetric
Fuel	PM_{10}	$PM_{2.5}$	Flaming phase
Wood A	95	91	111
Torrefied briquettes	40	32	69
Peat briquettes	214	210	230
Coal	189	185	313
Smokeless fuel	15	14	30

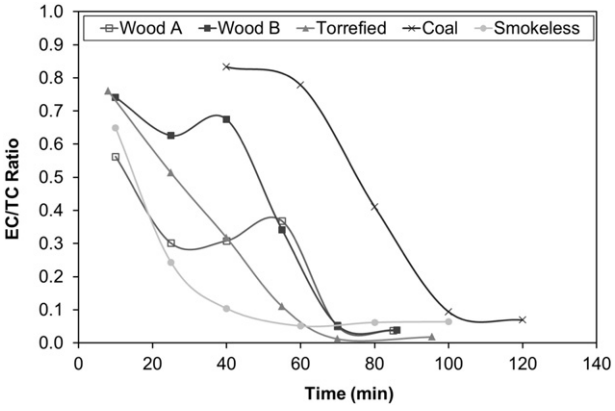

Fig. 9. Plot of EC/TC for (a) wood A (no. 1), □, (b) wood B (no. 2), ■, (c) torrefied wood (no. 3), ▲, (d) coal (no. 5), ×, and smokeless fuel (no. 8), ●.

Table 7
CO emission factors for the different combustion phases.

	ppm at 13% O_2		mg MJ^{-1}		
Fuel	Flaming	Smouldering	Flaming	Smouldering	Average over whole cycle
1	4817	14,372	5041	14,648	9845
2	2000	8112	2172	8507	4706
3	708	5553	781	5972	4084
4	2989	8779	3341	9688	5985
5	2334	12,229	2113	10,804	6941
6	2785	7417	2885	7629	6169
7	5078	15,495	4863	14,806	11,143
8	2775	9068	2518	8186	6853

with the concept that the formation of soot from coal and from biomass follows different routes [25,26].

Values for EC/TC were determined for five fuels, the two woods (nos. 1 and 2), the torrefied fuel (no. 3), the coal (no. 5) and the smokeless fuel (no. 8) during the combustion process. The data obtained are shown in Fig. 9.

The CO can be produced by the incomplete combustion of the volatiles in the flaming phase or from the combustion of the char in the smouldering phase; in both cases the CO is oxidised by the excess air to form CO_2 in the later stages of the combustor. In the case of rich homogeneous gaseous hydrocarbon flames there is a correlation between CO concentrations and soot yield (and also PAH because the formation routes are linked) and this is the case in the flaming phase. We find this is not the case since the CO emission during the smouldering phase is higher than the flaming phase-as shown by comparing Table 5 with Table 7. There is also considerable fluctuating combustion behaviour during the combustion process as observed by many others e.g. [17], this being due to the settling movement during the combustion of the fuel particles of char. The average concentrations during the different combustion phases for the different fuels are listed in Table 7. It is also interesting to note that the CO emission from the torrefied fuel is much lower than that from any of the other fuels.See Table 8

The level of CO emitted is dependent on the time temperature history above the burning bed and is characteristic of this type of unit. In particular the concentrations will be reduced if a secondary combustion chamber is fitted.

These values for CO, smoke and NO should be compared with the limits set in the UK [8] and in Europe [27] for small boilers. In the UK the RHI limits for new stoves (fitted with boilers, which is not the case here) are 30 g GJ^{-1} for particulate matter and 150 g GJ^{-1} NO_x. In the EU, whilst no limits have been agreed at present for small stoves or space heaters, values have been agreed for small boilers <59 kW where the limit for CO is 3000 mg m^{-3}at 10% O_2; organic compounds 100 mg $m^{-3}$and particulate matter 150 mg m^{-3}. Values have not been specified for NO_x. In order to achieve these limits for particulate emission a secondary combustion chamber would be necessary.

4. Discussion

4.1. The general features of biomass combustion

The factors determining combustion behaviour of biomass are: (1) the geometrical shape of the fuel, the porosity and the tendency of the fuel to undergo fragmentation. Here some fuels are in lump form of various sizes and others are briquetted. The external surface area of the fuel particle determines the rate of initial devolatilisation as well as the subsequent progress of the flame front into the particle and combustion of the char formed. These determine the burning rate and consequently the temperature in the combustion chamber, (2) the chemical composition—C, N and ash content and volatile content, and (3) the supply of air and operating conditions especially the fuel load which determines the fuel/air ratio.

Table 8
Comparison of previous results [10,11] mg MJ^{-1} with average results in this work given in parenthesis.

	Polish coal (Wujek) [15]	Lump pine wood
CO	2990 (6941)	2400 (4700)
NO_x	162 (204)	32 (140)
Particulate	294 (169)	116 (80)

The general features of the combustion of biomass and coal are generally understood [5,25,26,28] and there are many similarities such as the major steps of devolatilisation and char burn out. But there are some significant differences particularly in relation to the formation of smoke from biomass [25] compared with coal [26]. Many research groups have measured emission factors for various types of furnaces and it is not possible to list them all here. But only a few research groups have measured emission factors for both biomass and coal in the same appliances. The emission factors are approximately in accord with those observed in our previous work using biomass or coal and indeed co-firing [10,11], although for a slightly different furnace with a continuous feed and a secondary combustor. Such furnaces with continuous operation and secondary combustion chambers will emit lower levels of particulate matter, CO and organic material.

4.2. NO_x formation

The formation of NO_x can only be formed by the oxidation of fuel-N groups at the temperatures found here. The combustion of coal results in the formation of HCN [29]. In the case of biomass the fuel nitrogen compounds form both HCN and NH_3, but in the case of wood the majority of the product is HCN [22]. Consequently the straight line relationship shown in Fig. 5 might be expected since the chemical mechanism is similar and the rate of release of these compounds is determined by the mass burning rates; it is clear from Fig. 4 that they are not too dissimilar.

4.3. Particulate, organics and CO formation

The routes leading to the formation of smoke from biomass [25] and from coal [26] are different. In the former, pyrolysis of the different constituents, cellulose and lignin can form soot via the HACA (hydrogen abstraction–C_2H_2 addition) route or via aromatic compounds respectively. Coal mainly forms soot from the PAH and tar compounds released from the coal structure. However one feature is common and that is here they are all burning in the form of large particles which burn out slowly. It is seen from Fig. 4 that soot is released from both the flaming and most of the smouldering phases and it seems that volatiles or their secondary products are being released throughout the whole combustion cycle; indeed the amount of soot released is approximately proportional to the total mass of fuel burned. There are fragments of incompletely combusted fuel in the ash in both the case of biomass or coal based fuels as indicated in electron microscope photographs. Thus the mechanism we have previously put forward [5,10,11] and which is summarised in Fig. 10 would apply to both phases of combustion and for all the fuels studied here. The route via aromatic species would be dominant during the flaming phase and the smouldering route would be largely based on a HACA type route [5].

The smoke consists of carbonaceous particulates some of which have formed chains and agglomerated together with KCl aerosol and fragments of char. The data on size distribution shows that from this stove the majority of the particulate is below 2.5 μm. The formation of organic compounds such as PAH is an integral part of the soot forming mechanism and the ratio of the elemental carbon (EC) to the organic carbon (OC) is determined by the combustion chemistry of the volatiles produced by a particular solid fuel. The amount of OC bound to the EC particles depends on the initial VM and on the temperature history in the

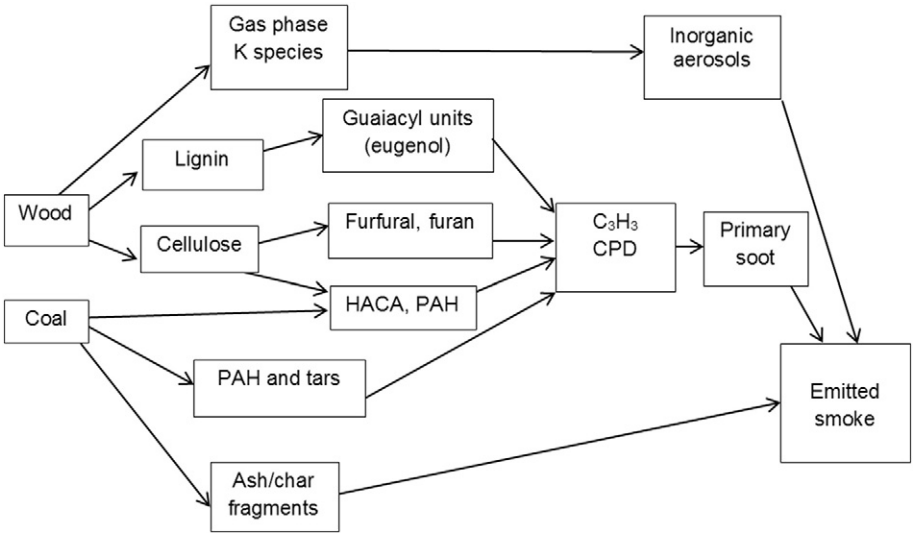

Fig. 10. The routes to the formation of smoke from biomass or coal, or a blend.

later stages of the furnace, as does the amount in the gas phase. The formation of CO follows a pattern depending on the phase of combustion. The initial stages of combustion involve devolatilisation from the outer layer of the particle releasing volatiles that then form both smoke and CO, both eventually forming CO_2 if the time–temperature conditions permit but the residence in most small units preclude this happening. In the smouldering phase the outer layer of the fuel particle will consist of char with some unreacted fuel decomposing in the core of the particle. The char will readily burn with the incoming oxygen producing greater quantities of CO and smaller amounts of smoke-as observed. The KCl will be equally released during both phases of combustion. Torrefaction of biomass has been found to reduce particulate emissions from combustion by approx. 40% compared to the source material, achieved by the reduction in volatile content.

Many researchers have stressed the importance of the ratio of Black Carbon (BC) to Organic Carbon (OC) in the combustion of carbonaceous fuels in relation to the impact on the climate. Effectively BC is equivalent to the elemental carbon (EC). The data in Fig. 9 shows that the values of EC/TC vary during the combustion cycle. In the operation of a real combustor it would be refuelled before it reaches the full extent of the smouldering stage and so here we have taken mean values of EC/TC from the flaming stage. These values are: wood A (no. 1), 0.4; wood B (no. 2), 0.6, torrefied wood (no. 3,) 0.4 and coal (no. 5), 0.8. In addition here we determine the averaged total particulate at two temperatures, namely at 170 °C and 70 °C. At the former temperature most of the OC would be lost giving a value of EC whilst at 70 °C most of it would be collected giving a value of the total amount of EC and OC which is effectively total carbon, TC. Here we find that for the main part of the combustion for wood A that EC/TC = 0.8 and for the torrefied wood and peat is 0.9; a smokeless fuel (no. 8) gave a value of 0.5. This method using selective condensation of the organic fraction depends on the volatility (and VM content) of the organic fraction released and varies from wood, torrefied wood and smokeless coal.

Measurements obtained using a similar combustion arrangement but using Aerosol Time of Flight Mass Spectrometry (ATOFMS) gave values of EC/TC of 0.4 for flaming and 0.3 smouldering for a soft wood [30]. A similar log fuelled combustion system although with two-stage combustion was found to give a value of EC/TC of 0.47 [31].

5. Conclusions

1. Eight fuels which included woods, torrefied fuels, coal and smokeless coal and which have substantial differences in their volatile content were burned as lumps in a single combustion chamber residential stove. The total particulate matter emissions (PM_t) associated with coal based fuels followed a linear relationship with the volatile content, the wood based fuels followed a different linear relationship whilst the single peat result was intermediate between the two classes. The torrefied fuel gave the lowest emission of the fuels studied. These arose because of the difference in the mechanism of soot formation of these fuels.
2. A linear relationship was found between the fuel-nitrogen content and the NO_x emitted for all fuels whether wood-based or coal-based. The wood fuels and torrefied wood briquettes showed the lowest NO_x emissions (<100 ppm at 13% O_2) due to the lowest fuel-bound nitrogen content. The levels of NO_x emissions from the coal-based fuels were approximately twice that of the wood fuels.
3. A cyclone set was used to determine the $PM_{2.5}$ and PM_{10} size fractions. It was found that the majority of particles are below $PM_{2.5}$ for all fuels whether wood-based or coal based. This was confirmed with SEM imaging and is consistent with the observations of other researchers.

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